

# **David Andress & Associates, Inc.**

**11008 Harriet Lane, Kensington, Maryland 20895      (301) 933-7179**

## **Air Quality and GHG Emissions Associated With Using Ethanol in Gasoline Blends**

**Prepared by:**

**David Andress**

**David Andress & Associates, Inc.  
11008 Harriet Lane  
Kensington, Maryland 20895**

**May 2000**

**Prepared for:**

**Oak Ridge National Laboratory / UT-Battelle, Inc.  
and  
Office of Fuels Development  
Office of Transportation Technologies  
Energy Efficiency and Renewable Energy  
U.S. Department of Energy.**

**Subcontract 11X-SY838  
Under Contract DE-AC05-96OR22464**

# Table of Contents

Overview and Summary .....	1
Background .....	4
Estimating Air Quality Impacts Associated with Motor Vehicle Emissions.....	5
Air Quality Concerns .....	7
Ozone .....	7
Air Toxics .....	7
Carbon Monoxide .....	8
Emissions From Ethanol Fuels Depend on Whether Ethanol is Blended with RFG or Conventional Gasoline.....	9
Conventional Gasoline.....	9
RFG Program .....	12
Nox Emissions .....	14
Toxic Air Emissions .....	15
Analysis of Acetaldehyde Emissions and Air Quality Changes for Ethanol Used in California RFG.....	19
Evaporative Emissions.....	20
Where Do Evaporative Emissions Come From? .....	230
How Does Adding Ethanol to Gasoline Affect RVP? .....	20
What is the Gas Tank Commingling Issue?.....	21
Where are the Problems and What Can Be Done to Control Higher Evaporative Emissions from Ethanol Blends?.....	23
Carbon Monoxide Emissions and Oxygenated Fuels .....	24
California Study on the Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline .....	27
Greenhouse Gas Emissions.....	28
The Fuel Cycle.....	28
GHG Emission Reductions .....	29

## Tables

Table 1. Directional Changes in Emissions When Ethanol is Blended with Conventional Gasoline and RFG .....	2
Table 2. Changes in Emissions When Ethanol is Blended at 10% in Conventional Gasoline .....	10
Table 3. Changes in Vehicular Primary Acetaldehyde Emissions Relative to 2003 MTBE Baseline Gasoline .....	17
Table 4. Comparison of Emission and Modeled Air Quality Changes for Primary Emissions of Acetaldehyde and Formaldehyde .....	18
Table 5. Comparison of Modeled Air Quality Changes from 1997 BTBE Baseline .....	19
Table 6. Comparison of Modeled Air Quality Changes from 2003 MTBE Baseline .....	19
Table 7. Percent Reduction in CO Emissions Resulting from 3.5% Oxygen, as Predicted by the MOBILE Model .....	25
Table 8. Reduction in Greenhouse Gas Emissions (grams/mile) from Ethanol Used in Ethanol Blends (% relative to gasoline, % range represents #10 to E95) .....	29

## Figures

Figure 1. Reid Vapor Pressure for Ethanol Blends .....	24
--	----

## Overview and Summary

This paper presents an overview of the issues related to air quality and greenhouse gas (GHG) emissions associated with ethanol used in gasoline blends. The air quality issues, in particular, are the subject of current regulatory interest because of the potential widespread replacement of MTBE with ethanol. The detection of MTBE in groundwater is growing, and a national debate about its continued use gasoline is currently taking place. The intent of this paper is to provide a short set of standalone topics that will provide a quick reference source for both federal and state government officials and the interested public. The reader is assumed to have some familiarity with the issues involved.

Estimating the impact of vehicular emissions on air quality is a complex science. It involves gathering data on tailpipe and evaporative emissions from each vehicle for each type of fuel used, estimating vehicle fleet characteristics and population driving patterns, and incorporating the effects of meteorological and geographic conditions to project the persistence of primary and formation of secondary emissions in the atmosphere.

The principal air quality concerns arising from gasoline-powered mobile-source emissions are ozone, toxic air pollutants, and carbon monoxide. The major ozone precursors come from emissions of volatile organic compounds (VOC) and nitrous oxides (NO<sub>x</sub>), and to a lesser extent carbon monoxide (CO). Because ozone formation is related to temperature and solar intensity, ozone problems occur primarily in hot weather. Toxic air pollutants are a year-round problem, but are more pronounced in hot weather. Carbon monoxide emissions from mobile sources are greater in cold weather, and unhealthy levels of CO are primarily a wintertime air quality problem.

Blending ethanol with gasoline produces changes in some emissions compared with straight gasoline and gasoline containing MTBE (see following table). The emission changes are related to whether ethanol is blended with conventional gasoline or RFG for several reasons. First, ethanol blended with conventional gasoline is granted a Reid Vapor Pressure (RVP) of one psi; the waiver does not apply to ethanol blended with RFG. Evaporative emissions increase with higher RVPs. Second, all RFG must meet the same compliance standards whether or not ethanol is present. For conventional gasoline blended with ethanol it is the underlying conventional gasoline that must meet the standards, subject to at-most a one-psi increase in RVP for the ethanol blend.

Most toxic air pollutants and other pollutants, except acetaldehyde, formaldehyde, and Peroxyacetyl nitrate (PAN), decrease when ethanol is added to gasoline, primarily through dilution. Formaldehyde emissions are lower for ethanol blends than for MTBE blends. Levels of formaldehyde, acetaldehyde and PAN are related to meteorological conditions, as much of the formation of these pollutants come from atmospheric transformations of other hydrocarbons referred to as secondary emissions. A California study on the air quality effects of ethanol concluded that acetaldehyde and PAN concentrations would increase only slightly for complying California RFG3 containing ethanol. (See section on acetaldehyde emissions for ethanol used in California RFG for details.) No comparable study has been done for Federal RFG or for non-California environments

EPA has observed that refiners have been exceeding the standards for toxic air reductions set forth by the RFG program. EPA attributes at least part of this over compliance to the use of oxygenates, i.e., ethanol and MTBE.

Adding ethanol to gasoline decreases emissions of CO, a product of incomplete combustion, in both conventional gasoline and RFG. In conventional gasoline, evaporative

VOCs increase due to the higher RVP of the ethanol mixture, and NOx emissions may increase because of the added oxygen. This does not happen in RFG, because VOC and NOx emissions must be controlled to meet RFG standards. The RVP increase from blending ethanol with gasoline is compensated for by producing a subgrade RFG with a lower RVP for ethanol blending.

Tier 2 regulations issued by EPA call for the nationwide introduction of lower sulfur gasoline (average of 30 ppm) beginning in 2004. The presence of sulfur in gasoline degrades the effectiveness of catalytic convertors. Ethanol reduces sulfur levels through dilution.

Like all gasoline blending components, ethanol has its advantages and disadvantages. Refiners must determine the most economic way of producing gasoline meeting environmental and driveability requirements. With limitations placed on MTBE use, refinery analyses show the use

**Table 1. Directional Changes in Emissions When Ethanol Is Blended with Conventional Gasoline and RFG**

**The Directional Changes Refer to Changes When Comparing Conventional Gasoline Containing Ethanol with Ethanol-Free Conventional Gasoline and RFG Containing Ethanol with RFG Containing MTBE.**

	Conventional Gasoline	RFG
<b>Toxic air pollutants</b>		
Acetaldehyde	increase	increase <sup>2</sup>
Benzene	decrease	decrease
1,3-butadiene	decrease	decrease
Formaldehyde	increase <sup>1</sup>	decrease
<b>Criteria air pollutants</b>		
CO	decrease	decrease
NOx	increase	no change
Tailpipe VOC	decrease	no change
Evaporative VOC	increase	no change
Total VOC	increase	no change
Particulate matter	decrease	decrease
<b>Other</b>		
PAN	increase	increase <sup>2</sup>
Isobutene	decrease	decrease
Toluene	decrease	decrease
Xylene	decrease	decrease
<sup>1</sup> Formaldehyde emissions decrease for ethanol blends compared with MTBE blends. <sup>2</sup> A California study concluded that the ambient air concentrations of acetaldehyde and PAN increased only slightly for California RFG3 containing ethanol, despite the fact that the increase in primary acetaldehyde emissions is significant. The study concluded that most of the increase in acetaldehyde and PAN concentrations were due to secondary emissions. No comparable study has been done for Federal RFG for areas outside California.		

of ethanol will be economic over a broad price range. Both ethanol and MTBE are high-octane, clean blending components, which will be at a premium if MTBE use is restricted. Ethanol's major disadvantage in summer RFG is its high blending RVP.

The problem of determining how emissions affect global warming differs from the problem of determining how emissions affect urban pollution in several important ways. First, the major GHG emissions are CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, are not regulated by EPA as contributors to urban air quality problems. Second, climate change is a global problem and must consider emissions from the total fuel cycle (feedstock production fuel conversion, and vehicle combustion). Urban pollution is a localized problem and EPA regulates only emissions associated with vehicle use.

Biomass fuels from ethanol emit no net carbon emissions from fuel combustion, since the carbon in the fuel is withdrawn from the environment during feedstock growth. The feedstock growth, fuel conversion, and feedstock and fuel transportation stages produce GHG emissions.

Corn ethanol used in E10 is currently estimated to reduce GHG emissions between 12 and 19 percent relative to gasoline, depending on whether wet or dry milling is used. GHG emission reductions for future corn ethanol are projected to be between 24 and 26 percent. The increase in GHG emission reductions is due to advances in farming practices and ethanol conversion technologies. For future cellulosic ethanol used in E10, reductions in GHG emissions are projected to be between 84 and 130 percent, depending on whether herbaceous or woody biomass is used. GHG reductions greater than 100% are explained by a coproduct credit for the sale of electricity from cellulosic ethanol plants.

## Background

Ethanol was first used as a motor vehicle fuel in 1908, but remained a small niche fuel favored by racers for many years. Beginning in the 1970s, several events occurred that led to the introduction of ethanol into the commercial gasoline market. Energy security concerns brought about by the Arab oil embargo spurred Congress to enact tax incentives to encourage the production of alternative fuels. Around the same time, concerns about environmental impacts associated with gasoline began to emerge. The banning of lead in gasoline created a demand for blending agents, like ethanol, with a high octane content. Ethanol demand further increased after Congress passed legislation requiring the use of oxygenates in gasoline to reduce harmful emissions from mobile sources. Global warming, considered the next major environmental front by many people, may further boost the demand for ethanol. Ethanol, being a renewable fuel, produces less GHG emissions than gasoline.

As part of a broad program to improve the nation's air quality, the Clean Air Act Amendments of 1990 (CAAA) impose requirements on fuels sold in urban areas with air quality problems. The CAAA requires the use of reformulated gasoline (RFG) in ozone nonattainment areas and oxygenated fuels in winter carbon monoxide nonattainment areas. The RFG program is designed to reduce mobile-source emissions that produce ozone and toxic air pollutants. The CAAA requires all RFG to contain an average of at least of 2.0 wt% oxygen and winter oxygenated fuels to contain an average of at least of 2.7 wt% oxygen. Most oxygen requirements are currently satisfied by either ethanol or methyl tertiary butyl ether (MTBE).

This paper focuses primarily on issues related to air quality and GHG emissions associated with ethanol used in blends (E10, E7.7, and E5.7). More than 99 percent of the ethanol currently consumed in the U.S. is in the gasoline blend market. Air quality issues related to ethanol used as a neat fuel (E85) are different, as the spectrum of evaporative and tailpipe emissions from neat fuels differs from those of blends. GHG emissions associated with ethanol used in blends and neat fuels are similar.

While comparisons with MTBE are necessary, no attempt is made to present a comprehensive treatment of MTBE. Both ethanol and MTBE have desirable properties that contribute to clean gasoline, but there are some important differences between them. In particular, the growing detection of MTBE groundwater contamination has prompted a national debate about its continued use. MTBE imparts a turpentine odor and taste to water at very low concentrations<sup>1</sup>.

---

<sup>1</sup> The health effects of MTBE in water are still being studied. MTBE has produced tumors at high doses in laboratory animals. At this time, insufficient data exists to determine if MTBE is a probable or known human carcinogen. (*Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*, p. 77 September 15, 1999)

## **Estimating Air Quality Impacts Associated with Motor Vehicle Emissions**

Estimating the impact of vehicular emissions on air quality is a complex science that involves developing sophisticated mathematical models, gathering reams of field data, and developing robust strategies for handling uncertainty. Listed below are some of the factors that enter into this process:

- Composition of vehicle fleet including the types of emission control technologies used and the number of poorly operating vehicles
- Driving patterns and population densities
- Type of fuel used
- Tailpipe and evaporative emissions from each vehicle
- Chemical pathways for secondary emissions
- Meteorological and geographic conditions
- Identification of emissions of concern and establishing monitoring programs

To illustrate what is involved in projecting air quality, consider the emissions from a single car. We fill the car with a type of fuel whose chemical composition is precisely known. We accompany this car throughout the day and monitor its evaporative and tailpipe emissions. The principal products of combustion are CO<sub>2</sub>, CO, NO<sub>x</sub>, and water. Unburned hydrocarbons are released into the atmosphere directly through evaporation or as they pass through the combustion chamber and the catalytic converter. Byproduct hydrocarbons can also be formed from incomplete combustion of gasoline components. The main compounds of interest, because of their potential adverse health impacts, include benzene and other aromatics, acetylene, 1,3-butadiene, and propylene.

That is for one car. Now we must do this for the entire vehicle fleet, using estimates of the fleet composition and expected driving patterns. EPA requires emission certification tests when manufacturers introduce new vehicle models. These tests provide emission profiles for the set of fuels on which they are certified. Emission models, such as the EPA Complex model or the California predictive model, are used to obtain emission profiles for proposed fuel formulations. As emission control systems typically experience some degradation with age, aging effects must also be taken into account. Also, EPA has long recognized that a small percentage of high polluters emit a disproportionate amount of air contaminants. Emission monitoring programs administered at the state level provide a valuable source of field data for statistically estimating these effects. However, as older cars are replaced by newer cars with advanced emission controls, a greater portion of the emissions will come from off road vehicles which are not subject to the same emission control standards and testing requirements.



Once released into the atmosphere, many combustion products and unburned hydrocarbons undergo chemical transformations. They may decompose into harmless molecules or may transform into so-called secondary air contaminants such as ozone, formaldehyde, acetaldehyde, and peroxyacetyl nitrate (PAN)<sup>2</sup>. The chemical transformations depend on meteorological conditions, such as temperature and solar intensity, and geographic conditions, such as altitude and the presence of surrounding mountains. Ultimately the atmospheric models have to be validated on field data collected from monitoring programs. Large quantities of field data exist for pollutants like CO, ozone, and NO<sub>x</sub>, and existing models have been calibrated with the empirical data. For other pollutants like acetaldehyde and PAN, which are especially associated with ethanol blends, insufficient field data exists. Lack of data for control conditions is also a problem (e.g., data before and after ethanol blends were introduced).

---

<sup>2</sup> Formaldehyde and acetaldehyde are both primary and secondary emissions.

## **Air Quality Concerns**

### **Ozone**

Ozone is a molecule consisting of three oxygen atoms that occurs naturally in the upper atmosphere and filters out harmful ultraviolet radiation from the sun. Ground-level ozone, on the other hand, is the major component of smog, which causes severe air quality problems in urban areas. Ozone is formed in the lower atmosphere through a complex set of chemical reactions involving hydrocarbons, oxides of nitrogen, and sunlight. Because the rate of ozone formation is related to both temperature and solar intensity, problematic ozone levels occur most frequently on hot summer afternoons.

Ozone is a harsh irritant that can cause stinging eyes, choking, coughing, and lung tissue damage. Exposure to high ozone levels may lead to respiratory infections in healthy individuals and is particularly harmful to people with existing respiratory diseases. Elevated ozone levels also inhibit plant growth and can cause widespread damage to crops and forests.

Unhealthy ozone levels are a problem across the United States, with nearly 100 cities exceeding the EPA National Ambient Air Quality Standard. Nine cities, home to 57 million people, are considered "severely" polluted, experiencing peak ozone levels that exceed the standard by 50% or more. In a typical urban area, more than half the emissions of hydrocarbons and nitrogen oxides come from cars, buses, trucks, and off-highway mobile sources. Ozone-forming emissions may be released into the atmosphere from fuel evaporation or through the tailpipe after fuel combustion. Controlling fuel volatility is particularly important for reducing evaporative hydrocarbon emissions.

### **Air Toxics**

Air toxics are air pollutants that cause adverse health effects. EPA has focused most of its air toxics efforts to date on carcinogens, but non-cancer health effects such as reproductive and neurological problems are also of concern. EPA classifies several pollutants emitted from motor vehicles as known or probable human carcinogens. Benzene is a known human carcinogen, while formaldehyde, acetaldehyde, 1,3-butadiene and diesel particulate matter are probable human carcinogens. EPA is also investigating whether oxygen-containing fuel additives such as MTBE cause adverse health effects.

Some toxic compounds are present in gasoline and are emitted to the air when gasoline evaporates or when it passes through the engine as unburned fuel. For example, small quantities of benzene, a component of gasoline, are emitted in unburned fuel or released to the atmosphere when gasoline evaporates.

Incomplete combustion of compounds in gasoline causes a significant amount of automotive emissions. Benzene, for example, is formed from the incomplete combustion of toluene and xylene, which are chemically similar to benzene. Like benzene, these compounds occur naturally in petroleum and become more concentrated when petroleum is refined to produce

gasoline. Formaldehyde, acetaldehyde, particulate matter, and 1,3-butadiene are not present in fuel but are by-products of incomplete combustion.

Formaldehyde and acetaldehyde are also formed through a secondary process when other mobile source pollutants undergo chemical reactions in the atmosphere. PAN, which is an eye irritant and harmful to plants, is also formed primarily through atmospheric transformation. The rate of atmospheric transformation of these secondary emissions depends on meteorological conditions.

### **Carbon monoxide**

Carbon monoxide (CO) is a colorless, odorless, poisonous gas produced from the incomplete burning of hydrocarbon-based fuels. It enters the bloodstream through the lungs and forms carboxyhemoglobin, a compound that inhibits the blood's capacity to carry oxygen to organs and tissues. Carbon monoxide can affect healthy individuals by impairing exercise capacity, visual perception, manual dexterity, learning functions, and ability to perform complex tasks. Individuals with respiratory and vascular problems are especially sensitive to carbon monoxide poisoning and may experience chest pain if they breathe the gas while exercising.

## **Emissions From Ethanol Fuels Depend on Whether Ethanol is Blended with RFG or Conventional Gasoline**

The emission changes associated with using ethanol in gasoline depend on whether ethanol is blended with RFG or with conventional gasoline. There are several reasons for this. First, RFG must meet a stricter set of specifications for reducing emissions than conventional gasoline, and these standards apply equally to ethanol and non-ethanol blends. For ethanol blended with conventional gasoline, the standards apply to the conventional gasoline before it is blended with ethanol. Second, conventional gasoline containing 10 percent ethanol is granted a one-psi Reid Vapor Pressure (RVP) waiver. The waiver does not apply to RFG containing ethanol. The lower RVP of RFG ethanol blends is believed to account for much of the differences in directional changes in the emission profiles when comparing conventional gasoline and RFG ethanol blends to ethanol-free conventional gasoline and RFG, respectively. For example, total VOC emissions increase when ethanol is blended with conventional gasoline compared with straight conventional gasoline due to of the increased evaporative emissions resulting from the higher RVP of the ethanol blend. RFG, on the other hand, is VOC-controlled, and the VOC emissions of RFG blended with ethanol must meet the same standards of ethanol-free RFG.

### **Conventional Gasoline**

The directional changes in emissions when ethanol is blended with conventional gasoline are shown in the following table. An RVP waiver of one psi is assumed for a 10 percent ethanol blend. The second column of the table shows the directional changes in the emissions. The third column shows changes published in a 1991 Air/Oil Technical Bulletin. A 1998 University of California review of E10 emissions arrived at similar estimates. The actual emission changes are related to vehicular engine and emission control technology. The fourth column shows model-predicted emission changes made by the Canadian Natural Resource Council (NRC).

**Table 2. Changes in Emissions When Ethanol is Blended at 10% in Conventional Gasoline**

	Directional Change	Auto/Oil <sup>1</sup> (percent change)	NRC of Canada <sup>2</sup> (percent change)
Toxic air pollutants			
Acetaldehyde (primary)	increase	159.0 Å 43.6	28-36%
Acetaldehyde (secondary)			
Benzene	decrease	-11.5 Å 6.0	
1,3-butadiene	decrease	-5.8 Å 5.7	
Formaldehyde (primary)	increase	19.3 Å 31.2	10-28%
Formaldehyde (secondary)			
Criteria air pollutants			
CO	decrease	-13.4 Å 4.9	-15
NOx	increase	5.1 Å 4.1	0
Tailpipe VOC	decrease	-5.9 Å 2.7	
Evaporative VOC	increase		
Total VOC	increase		9
Particulate matter	decrease		
Other			
PAN (secondary)	increase		12-18%
Isobutene	decrease		
Toluene	decrease		
Xylene	decrease		

<sup>1</sup> Auto/Oil Air Quality Improvement Research program, Technical Bulletin No. 6, "Emission Results of Oxygenated Gasolines and Changes in RVP", 1999

<sup>2</sup> Singleton, D.L., A. Britton, W. Jiang, and R. McLaren (1997) "E10 Ethanol-Gasoline and the Formation of Tropospheric Ozone and Secondary Organic Species," National Research Council Report PET-1384-96S prepared for Air and Waste Section, Health Protection Branch, Health Canada, Ottawa, Canada, July 11.

Adding ethanol to conventional gasoline reduces tailpipe emissions of volatile organic compounds (VOC). However, total VOC emissions increase, because the decrease in tailpipe VOC emissions is more than offset by the increase in evaporative VOC emissions. This is due to the one-psi RVP waiver for conventional gasoline containing 10 percent ethanol. This situation does not happen with RFG, because all RFG must meet the same VOC emission standards whether or not it is blended with ethanol.

The decrease in CO and increase in NOx are due to the added oxygen. Ethanol fuels increase acetaldehyde, formaldehyde, and PAN emissions relative to pure gasoline. The large increase in acetaldehyde emissions must be put into context that the levels of acetaldehyde emissions are small compared to other toxic pollutant emissions. Formaldehyde emissions decrease when compared with gasoline containing MTBE. Decreases in other emissions, such as benzene, 1,3-butadiene, toluene, and xylene, are caused primarily by dilution.

The Canadian NRC study estimated that the use of E10 with a one psi RVP increase would increase concentrations of ozone (0.4 to 1.6%), formaldehyde (1.0 to 1.5%), acetaldehyde (about 2.7%), and PAN (2.9 to 4.5%), and an approximate 15% reduction in CO concentrations, relative

to industry-average gasoline. Estimates of a 159% increase in primary acetaldehyde emissions have to be compared to the (1.0 to 1.5%) increase in acetaldehyde atmospheric concentration. The light-duty gasoline vehicle contribution to the 24-hour-average secondary formaldehyde and acetaldehyde concentrations was 10 to 18% and 28 to 36% greater, respectively, for the ethanol blend. The light-duty gasoline vehicle contribution to PAN was 12 to 18% greater for the E10 gasoline than that for industry-average gasoline.

## **RFG Program**

The CAAA requires the use of RFG in extreme or serious ozone nonattainment areas and provides an option to use RFG in areas with moderate or marginal ozone nonattainment problems. EPA requires RFG to meet a set of specifications that will reduce emissions of VOCs, NO<sub>x</sub>, and toxic air pollutants a specified percent from a given baseline. The reductions are greater in the summer when ozone-causing smog problems are worse. While refiners have considerable leeway in developing a fuel formulation to meet the emissions standards, all RFG must contain an average oxygen content of at least 2.0 weight-percent, and cannot contain more than 1.0 volume percent of benzene. EPA uses its Complex model to determine if a proposed fuel formulation meets the RFG emission standards.

Oxygenates like ethanol and MTBE are valuable blending components. They provide a clean source of high octane that helps reduce emissions of toxic air pollutants and carbon monoxide. While a major goal of the RFG program is to reduce mobile emissions that are classified as ozone precursors, the Complex model currently gives credit in this area primarily to reductions of VOC and NO<sub>x</sub> emissions. A 1999 Natural Research Council (NRC) report found that CO emissions are a major contributor to ozone and that oxygenates help reduce CO emissions. The report recommended that EPA should recognize this fact in the Complex model. Both EPA and the state of California have since proposed to incorporate an oxygenate adjustment in their emissions models to account for this effect.

VOC emissions arise through the combustion of gasoline (tailpipe emissions) and from evaporation (evaporative emissions). MTBE has an advantage over ethanol in summer RFG, because adding ethanol to gasoline raises the RVP of the mixture. This causes an increase in evaporative VOC emissions that must be compensated for by producing a low-RVP subgrade gasoline for ethanol blending. This situation occurs only in the summer, because wintertime VOC requirements for RFG are not constraining. For refinery modeling, the choice of which oxygenate to use in RFG is largely an economic one and depends on the prices of ethanol and MTBE. No matter which oxygenate is used, VOC standards for RFG must be met. In reality, logistics issues such as the availability of terminal storage and blending equipment play a role in determining whether ethanol is used.

With the growing concern over MTBE contaminated groundwater, reductions in MTBE use are likely. In 1999, the state of California enacted legislation to phase MTBE out California gasoline by the end of 2002. These events have prompted a reexamination of the contributions of oxygenates in meeting the emissions reductions required by the RFG program. Opinions differ about whether the RFG oxygen requirement should be maintained.

Refiners argue that the RFG oxygen requirement is not necessary and that they should be given flexibility producing gasoline that meets the RFG emissions reduction standards. California refiners have produced some oxygen-free gasoline that meets California RFG specifications, which are even stricter than Federal RFG specifications. The 1999 NRC report also concluded that oxygenates are not needed to meet VOC emission standards. However, the NRC report did not consider the full spectrum of the RFG program, such as reductions in toxic air pollutants.

EPA has observed that toxic air pollutant reductions achieved in practice were greater than those required by the RFG standards. EPA attributes much of this over compliance to the use of oxygenates. This conclusion was based on a statistical analysis of field data and on model simulations of fuels containing different oxygen concentrations. This has led to questions about whether the removal of the RFG oxygen requirement would result in a substantial loss of this over compliance. Nonetheless, an EPA Blue Ribbon Panel on Oxygenates recommended that the RFG oxygen mandate be repealed, but added that "no backsliding" regulations should be put into effect to maintain the over compliance in toxic reductions.

While the refiners are arguing for the removal of the oxygen mandate, they are not advocating the removal of oxygenates from gasoline. They want the flexibility to determine the amount of oxygenates to use. Refinery modeling done for the Department of Energy (DOE), the state of California, and the National Petroleum Council (NPC) have all concluded that, even if the oxygen mandate were removed, the use of oxygenates is an economic way of producing gasoline. The amount and type of oxygenates used will depend on the prices of ethanol, MTBE, and petroleum inputs. If MTBE use were restricted, a substantial amount of ethanol would be cost effective to use over a broad range of ethanol prices. The NRC report was deficient in failing to recognize the role that oxygenates would still play if the RFG oxygen requirement were removed. In fact, questions have been raised about the cost effectiveness of producing only oxygenate-free gasolines.

Why is this so? Oxygenates are a clean source of octane. If oxygenates were not used, they would have to be replaced with other high octane sources such as aromatics and alkylates. Adding more aromatics is not desirable because they increase emissions of toxic air pollutants. Alkylates are considered a better alternative, but investments are needed to increase alkylation capacity. Oxygenates currently make up about 4% (MTBE 3% and ethanol 1%) of the U.S. gasoline pool. If oxygenates were totally removed from gasoline, additional petroleum refinery capacity would be needed to make up the volume shortfall. This would be on top of projected increases in gasoline demand, which are already expected to strain domestic refinery capacity. Because U.S. refinery margins are currently very low, refiners have been hesitant to make investments for major expansions. No new refineries have been built in the U.S. since the 1970s.

The upcoming requirement for low sulfur gasoline may also increase the demand for oxygenates. Sulfur degrades the effectiveness of catalytic converters in existing vehicles and can affect the ability of future automobiles – especially those designed for very low emissions – in meeting more stringent emissions standards. EPA has issued regulations that will limit the average sulfur content in all gasoline sold in the U.S. to 30 ppm. Sulfur content in gasoline outside of California currently averages about 330 parts per million (ppm). California gasoline must already meet low sulfur requirements and the California Air Resources Board (CARB) is proposing even lower limits. Oxygenates can contain lower levels of sulfur than gasoline, and their use as a blending agent reduces sulfur concentrations through dilution. Before denaturants are added, the sulfur content of ethanol is typically very low, e.g., about 1 to 3 ppm for corn ethanol produced by wet millers. The sulfur content of merchant ethanol is determined primarily by the sulfur content of the denaturant<sup>3</sup>.

---

<sup>3</sup> Under current denaturing practices another 15 to 47 ppm may be added via denaturant. Even when low sulfur gasoline of 30 ppm is available, ethanol would still contain 2-5 ppm sulfur after denaturing.



Refinery modeling encompasses simulating the full spectrum of refinery products, including the production of both RFG and conventional gasoline. The models determine how to process the petroleum inputs and allocate the derived petroleum fractions to finished products meeting regulatory standards<sup>4</sup> in a least cost manner. Removal of the RFG oxygen mandate provides additional flexibility for using oxygenates in conventional gasoline, and this offers an opportunity for alternative allocations of petroleum fractions. Since a 10-percent ethanol conventional gasoline blend is granted a one-psi RVP waiver, some ethanol that would have gone into RFG may be more economically blended into conventional gasoline. This gives the refiner an opportunity to move some higher-octane, low-RVP components that would normally have gone into conventional gasoline into RFG.

## **NOx Emissions**

NOx is an ozone precursor and a contributor to acid rain. Opinions differ about whether NOx emissions increase with the addition of fuel oxygenates and whether air quality will be affected. EPA maintains that for complying RFG, its Complex Model shows no increase in NOx emissions when the oxygen concentration is increased from 2.0 to 2.7 weight percent (40 CFR Part 80). EPA also maintains that increasing the oxygen level to 3.5 weight percent will not increase NOx emissions. EPA analysis suggests that NOx emission changes when oxygenates are added are related to aromatic levels. (NOx emissions tend to increase when ethanol is added to conventional gasoline. RFG typically contain lower levels of aromatics than conventional gasoline.) EPA notes that others may disagree with this conclusion and that some experimental data show that NOx emissions increase. EPA recognizes that some states may conclude that lower maximum oxygen limits are needed to maintain air quality and allows a state to request lower maximum oxygen levels for VOC controlled gasoline. Such a request had been approved for California, but California has rescinded their oxygen cap and now permits 3.5 wt% oxygen for ethanol blends. California was separately granted a variance for the wintertime oxygenated fuels program that reduces the oxygen content requirement from 2.7 wt% to 2.0 wt% for wintertime fuels used in carbon monoxide nonattainment areas.

Refinery modeling suggests that the cost of controlling NOx emissions in VOC-controlled RFG at higher oxygen concentrations can depend on the RFG share of the gasoline production. This situation is illustrated by the difference between California and the rest of the country. All California gasoline must meet California's unique RFG standards and consequently is not interchangeable with gasoline sold outside California<sup>5</sup>. California RFG is produced almost solely by California refineries, which produce little conventional gasoline. This constrains their ability to move blendstocks between conventional gasoline and RFG pools. In the rest of the country, the conventional gasoline share is much greater than the RFG share, giving refiners more flexibility in moving blendstocks that help reduce NOx emissions into RFG.

---

<sup>4</sup> Regulatory requirements include both RFG standards and anti-dumping regulations for conventional gasoline.

<sup>5</sup> For operational reasons, some California RFG is sold outside of California.

## Toxic Air Emissions

Oxygenates like ethanol and MTBE help reduce some toxic air pollutants through dilution. The directional changes in toxic air reductions when ethanol is added are similar to those in conventional gasoline. However, differences between conventional gasoline and RFG ethanol blends can affect the degree of toxic air reductions. Refiners produce an optimized subgrade RFG for blending with ethanol. The composition of this subgrade RFG will not be the same as a subgrade RFG for blending with MTBE. It is the final RFG, whether blended with ethanol or MTBE, that must meet the RFG standards for reduced toxic emissions. Historically, an optimized subgrade gasoline was not produced for blending ethanol with conventional gasoline. However, refiners have begun producing subgrade gasolines for ethanol blending in Minnesota and several other areas. Minnesota has a state-imposed year-round oxygen-content requirement.,

As discussed above, refiners have been producing RFG that exceeds the RFG toxic emission standards. EPA attributes at least part of this over compliance to the use of oxygenates.

On the other hand, oxygenates can increase some toxic air emissions. For ethanol, the primary emission of concern is acetaldehyde; for MTBE, it is formaldehyde. PAN emissions may also increase with ethanol use. PAN is not classified as a toxic air emission by EPA, but is a health concern. Because of the potential for widespread replacement of MTBE in RFG with ethanol, questions have been raised about the possibility of increases in acetaldehyde and PAN emissions. The state of California has studied this issue and determined that the use of ethanol in complying California RFG3 will have minimal effects on acetaldehyde and PAN concentrations and would result in a small reduction in formaldehyde emissions. The latter conclusion is due to the elimination of MTBE. Most of the California air quality modeling was for the summer season, when ozone problems are worse. See the section on "California Study on the Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline" for more information.

No comprehensive study has yet been done for Federal RFG. The results of the California study suggest that problems with increased in acetaldehyde and PAN emissions may not exist for complying Federal RFG. But some differences do exist between California and the rest of the country, and these must be taken into account. First, California RFG3 standards are stricter than Federal RFG2 standards. A big difference between the two is the current low sulfur standard for California RFG. However, Federal low-sulfur standards for all gasoline will be phased between 2004 and 2006, reducing some of the differences between California and Federal RFG. Second, the California air quality modeling was done for meteorological conditions in California. Meteorological conditions in other parts of the country have to be explicitly considered in atmospheric models. Lastly, the California findings do not apply to ethanol blended with conventional gasoline, which is granted a one-psi RVP waiver. This increases evaporative emissions hydrocarbons and ethanol which may form acetaldehyde, formaldehyde, and PAN through atmospheric transformations. The extent of this effect has not been adequately studied.

## **Analysis of Acetaldehyde Emissions and Air Quality Changes for Ethanol Used in California RFG**

The major products of concern for increased ethanol use in gasoline blends are acetaldehyde and PAN. A recent California study<sup>6</sup> looked at the air quality impacts of these pollutants for gasoline meeting California RFG 3 standards in the South Coast (Los Angeles) basin. Their approach used state-of-the-art airshed models that incorporated projected vehicular emission profiles and atmospheric chemical transformations. The study concluded that other components of gasoline, such as aromatic compounds and olefins, are primarily responsible for the formation of formaldehyde, and PAN due to both their greater abundance in gasoline and their shorter atmospheric lifetimes.

Compared with the 1997 MTBE baseline gasoline, the study concluded that atmospheric levels of acetaldehyde are predicted to increase (4%) for ethanol-blended gasoline at 3.5 wt% oxygen and decrease (-6%) for ethanol-blended gasoline at 2.0 wt% oxygen. PAN levels are not predicted to increase for either the ethanol-blended or non-oxygenated gasolines.

Acetaldehyde is both directly emitted from vehicular combustion and formed from atmospheric transformation of ethanol and other hydrocarbons. The rate of acetaldehyde formation and decomposition depends on meteorological conditions. Understanding how all these factors work together is needed to estimate changes in atmospheric levels of acetaldehyde. The California report is the only comprehensive analysis of acetaldehyde air quality impacts related to ethanol published to date. The findings from that report should be interpreted within the context of the study premises. This section is more technical than the rest of this paper, but it also gives a flavor of the difficulty involved in estimating air quality changes related to fuel formulation.

The California study compares differences in emissions and air quality levels between complying California gasoline containing MTBE, ethanol, and no oxygenates. Both the 1997 and 2003 baseline MTBE fuels meet CARFG 2 standards. The 1997 MTBE baseline gasoline is representative of gasoline used in 1997; the 2003 MTBE baseline gasoline assumes further emission reductions are achieved. Two ethanol concentrations were analyzed, one containing 2.0 wt% oxygen (E5.7) and one containing 3.5 wt% oxygen (E10). Both ethanol blends and the non-oxygenated gasoline meet the CARFG3 standards.

The following table lists the percent changes in primary acetaldehyde emissions for ethanol blends and non-oxygenated fuel relative to 2003 baseline MTBE gasoline.

---

<sup>6</sup> *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline*, December 1999, California Environmental Protection Agency, Air Resources Board

**Table 3. Changes in Vehicular Primary Acetaldehyde Emissions Relative to 2003 MTBE Baseline Gasoline**

Scenario / Type of Change	Percent Change
2003 Ethanol at 2.0 wt% Oxygen	27%
2003 Ethanol at 3.5 wt% Oxygen	132%
2003 Non-Oxygenate	-5%
<i>Source: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline, December 1999, California Environmental Protection Agency, Air Resources Board</i>	

To separately track changes in air quality associated with primary and secondary emissions, the air-shed photochemical models treat each of these categories as distinct species. The air quality changes reported for the primary acetaldehyde emissions, for example, apply only to the emission concentrations of the primary acetaldehyde emissions, not to the total atmospheric acetaldehyde concentrations. The total air quality changes are a weighted combination of the primary and secondary air quality changes, where the weighting factors are the relative contributions of the primary and secondary emissions, respectively

The air-shed photochemical models track primary and secondary emission changes from all mobile and stationary sources, of which emissions from gasoline-fueled vehicles are a part. The acetaldehyde emission statistics presented below refer to emissions associated with all sources.

Changes in primary emissions of acetaldehyde and formaldehyde and the impacts on air quality for different fuel formulations are listed in the following table. The second and third columns show changes relative to the 1997 MTBE baseline; the fourth and fifth columns show changes relative to the 2003 MTBE baseline. Compared to the 1997 MTBE baseline gasoline (column 2), the relative improvement in air quality is greater than the percent decrease in acetaldehyde emissions, except for the 3.5 wt% ethanol blend. In this latter case the relative deterioration in air quality is less than the percent increase in acetaldehyde emissions. Air quality is measured as a population-weighted daily concentration of acetaldehyde emissions. Negative air quality changes denote lesser emission concentrations or improvements. This difference between emission and air quality changes emphasizes the need to take into account factors such as atmospheric persistence.

**Table 4. Comparison of Emission and Modeled Air Quality Changes for Primary Emissions of Acetaldehyde and Formaldehyde**

	Changes From 1997 MTBE Baseline		Changes From 2003 MTBE Baseline	
	Acetaldehyde	Formaldehyde	Acetaldehyde	Formaldehyde
Scenario / Type of Change	(Primary)	(Primary)	(Primary)	(Primary)
<b>2003 Baseline Inventory (MTBE-based CaRFG2)</b>				
Emissions	-12%	-13%	--	--
Air Quality <sup>a</sup>	-25%	-25%	--	--
<b>2003 Ethanol Blend at 2.0 wt% Oxygen</b>				
Emissions	-6%	-15%	6%	-2%
Air Quality <sup>a</sup>	-23%	-27%	4%	-3%
<b>2003 Ethanol Blend at 3.5 wt% Oxygen</b>				
Emissions	15%	-15%	30%	-3%
Air Quality <sup>a</sup>	4%	-27%	39%	-3%
<b>2003 Non-Oxygenate</b>				
Emissions	-13%	-16%	-1%	-4%
Air Quality <sup>a</sup>	-26%	-27%	-1%	-4%
<sup>a</sup> Air quality changes are based on changes in population-weighted daily-average model results for a gridded region. Negative changes mean improvements.  <i>Source: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline, December 1999, California Environmental Protection Agency, Air Resources Board</i>				

Compared to the 2003 MTBE baseline gasoline (column 4), the changes in emission levels and air quality impacts from primary acetaldehyde emissions are relatively small for the 2.0 wt% ethanol blend (6% and 4%, respectively), but significant for the 3.5 wt% ethanol blend (30% and 39%, respectively). However, as shown below, their impact on the total (primary and secondary emissions) changes in air quality is small, since most of the atmospheric acetaldehyde arises from secondary transformations. The changes in formaldehyde emissions and air quality (columns 3 and 5) are listed for comparison.

The following tables show the air quality changes for total, and from both primary and secondary, acetaldehyde emissions for the non-MTBE gasolines. The first table shows changes from the 1997 MTBE baseline gasoline, while the second table shows changes from the 2003 MTBE baseline gasoline. In all cases, the total impact on air quality from acetaldehyde

emissions is predominately determined by the secondary acetaldehyde emissions. Of particular note is the 3.5 wt% ethanol blend compared to the 2003 MTBE baseline gasoline. The change in air quality from primary acetaldehyde emissions is a sizeable 39%, but the change in air quality from secondary emissions is only 2% and the total in air quality is 4%. That is, the 39% change in air quality from primary acetaldehyde emissions – which is due to a 132% increase in vehicular acetaldehyde emissions – is approximately equivalent to a 2% change in air quality from secondary acetaldehyde emissions. This example illustrates the need to consider the changes in total ambient air quality and not just the changes in vehicular emissions.

**Table 5. Comparison of Modeled Air Quality Changes from 1997 MTBE Baseline**

Compound	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
<b>Acetaldehyde (Total)</b>	<b>-13%</b>	<b>-13%</b>	<b>-10%</b>	<b>-14%</b>
<b>Acetaldehyde (Primary)</b>	<b>-25%</b>	<b>-23%</b>	<b>4%</b>	<b>-26%</b>
<b>Acetaldehyde (Secondary)</b>	<b>-12%</b>	<b>-12%</b>	<b>-11%</b>	<b>-13%</b>
Air quality changes are based on changes in population-weighted daily-average model results for a gridded region. Negative changes mean improvements.  <i>Source: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline, December 1999, California Environmental Protection Agency, Air Resources Board</i>				

**Table 6. Comparison of Modeled Air Quality Changes from 2003 MTBE Baseline**

Compound	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
<b>Acetaldehyde (Total)</b>	<b>0%</b>	<b>4%</b>	<b>-1%</b>
<b>Acetaldehyde (Primary)</b>	<b>4%</b>	<b>39%</b>	<b>-1%</b>
<b>Acetaldehyde (Secondary)</b>	<b>0%</b>	<b>2%</b>	<b>-1%</b>
Air quality changes are based on changes in population-weighted daily-average model results for a gridded region. Negative changes mean improvements. <i>Source: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline, December 1999, California Environmental Protection Agency, Air Resources Board</i>			

## **Evaporative Emissions**

Evaporative emissions are caused by the release of hydrocarbons and oxygenate into the atmosphere due to the inherent volatility of the fuel. The tendency of a fuel to vaporize is measured by its Reid vapor pressure (RVP). A higher RVP rating indicates a more volatile fuel, but the actual rate of vaporization is related to temperature. Higher temperatures increase evaporative emissions. For driveability, winter gasoline has a higher RVP to aid in cold starts, and summer gasoline has a lower RVP to limit vapor locks. For environmental reasons, summer gasoline sold in ozone nonattainment areas has an even lower RVP to reduce evaporative VOC emissions.

### **Where Do Evaporative Emissions Come From?**

Evaporative fuel losses associated with motor vehicle operation can be described by the following four processes:

- Refueling
- Running loss – emissions losses occurring during operation of the vehicle. Most of the losses are due to permeation through the fuel hoses and losses from the carbon canister, a container filled with sorbent activated carbon used to store gasoline vapors.
- Hot soak – vapor losses from a recently operated hot vehicle. Most of these losses are due to permeation through hoses.
- Diurnal – emissions arising mainly from the charcoal canister. They result from daily heating of the vehicle's fuel tank and consequent saturation and overflow from the canister.

### **How Does Adding Ethanol to Gasoline Affect RVP?**

The addition of ethanol to gasoline can result in a mixture with an RVP that is greater than the RVP of pure gasoline or pure ethanol. This effect is most pronounced in low-level ethanol blends, as shown in the accompanying figure. For example, adding ethanol to a gasoline with a 9-psi RVP results in a mixture with an RVP of approximately 10 psi, even though the RVP of pure ethanol is only 2.3 psi.

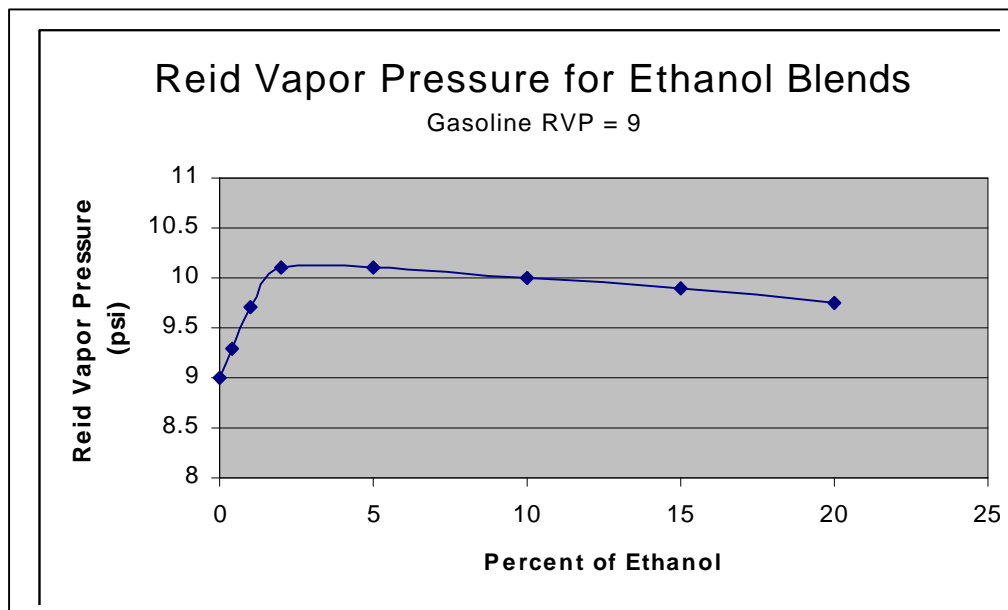
A 10-percent blend of ethanol with conventional gasoline is granted an RVP waiver of one psi, which corresponds roughly to the RVP increase of the mixture. The waiver does not apply to ethanol blended with RFG. To use ethanol in summer RFG, refiners have to produce a lower RVP subgrade RFG for ethanol blending. This usually entails removing some of the butanes or pentanes, which account for more than 70 percent of the evaporative emissions in pure gasoline.

### What is the Gas Tank Commingling Issue?

When an ethanol blend is mixed with ethanol-free gasoline, the RVP of the mixture is determined as if the base gasoline of the ethanol blend is combined with the ethanol-free gasoline and the ethanol is then

added to the mixture. Consider a 50-50 commingled blend of a 10 percent RFG ethanol blend with ethanol-free RFG, both of which have an RVP of 7.0 psi. For this to happen, the RVP of the gasoline portion of the ethanol blend has to be about 6.0 psi to account for the 1.0 psi increase when ethanol is added. Thus, the RVP of the gasoline portion of the commingled blend is about 6.5 psi (simple averaging), and the ethanol concentration is 5 percent. Because the 5 percent ethanol content increases the RVP by about 1.0 psi, the RVP of the commingled blend is about 7.5 psi. This example illustrates the basic principal involved, but the actual increase may differ in reality. For instance, the presence of cosolvents, such as MTBE, will reduce the RVP increase.

Because gasolines containing ethanol and ethanol-free are kept separate in the distribution system, the commingling problem is confined to consumer gas tanks. The extent of the problem is related to such things as ethanol blend market share, brand loyalty, and the distribution of fuel tank levels before and after a refueling event. One study estimated an increase in the average RVP for RFG would be between 0.1 and 0.3 psi, depending upon the assumptions for the proceeding factors<sup>7</sup>. The study concluded that the RVP increase from commingling would be at a maximum when the ethanol market share is between 30 and 50 percent. At the present time, ethanol is used in RFG only in the Chicago / Milwaukee area and almost exclusively so. Consequently, no commingling problems exist.



<sup>7</sup> Peter Caffrey and Paul Machiele, "In-Use Volatility Impact of Commingling Ethanol and Non-Ethanol Fuels," SAE Technical Paper #94065, February 29, 1994. See also, "The Octamix Waiver," 53 FR 3636, February 8, 1988.



When a conventional gasoline ethanol blend is commingled with an ethanol-free conventional gasoline, the RVP of the commingled blend is typically the same as the RVP of the ethanol blend. This happens because the conventional gasoline ethanol blend has a one-psi RVP waiver. The RVP of base gasoline in the ethanol blend is about the same as the RVP in the ethanol-free gasoline. A greater issue for conventional gasoline is the ethanol market share, since the greatest RVP increase of the gasoline pool occurs when all conventional gasoline contains ethanol. Whether this presents air quality problems depends on where the gasoline is used. Most conventional gasoline is used in areas that are not classified as having ozone problems. However, for areas with borderline air quality problems, the RVP increase from ethanol conventional gasoline blends could be an issue.

## **Where are the Problems and What Can Be Done to Control Higher Evaporative Emissions from Ethanol Blends?**

### ***Upgrade Evaporative Emission Control Systems on Motor Vehicles***

EPA requires automobile manufacturers to certify their emission control systems on a prescribed set of fuels. Except for ethanol flex fueled vehicles (FFV), gasoline-powered motor vehicles are not required to certify their evaporative emission control systems on ethanol fuels. FFVs are required to certify their evaporative emission systems on pure gasoline, E10 (highest RVP), and E85.

Ethanol-containing gasolines may lead to increases in evaporative emissions because rubber, plastics, and other materials are more permeable to smaller ethanol molecules. It also has been suggested that, because of its propensity to be tightly held by activated carbon in conjunction with its hygroscopic nature (attracts water), ethanol may reduce the working capacity of the charcoal canisters used to control evaporative emissions. However, the data behind this conclusion is considered inconclusive and more research is needed.

The upgraded evaporative control systems used on FFVs include a larger canister containing a greater volume of carbon, sensors to increased purge control capacity, and upgrades to materials used in the fuel pump and fuel lines. The additional cost of a FFV compared with a standard vehicle has been estimated at around \$160. This includes upgrades to the evaporative emissions system, the gasoline supply system, and oxygen fuel sensors that monitor the ethanol-gasoline ratio

EPA has been concerned that, over time, alcohol-containing fuels could degrade the nonmetallic components of a vehicle's gasoline supply system. In particular, the permeability of cheaper elastomer components could increase over time, which could lead to an increase in evaporative emissions. EPA Tier 2 regulations, will require manufactures to use E10 during the durability cycle, a process that can be likened to driving a vehicle 50 or 100 thousand miles to age components. The vehicle is then certified to meet emission standards on gasoline, not E10.

### ***Develop RVP-Reducing Additives***

Several companies are trying to develop additives to reduce or eliminate the RVP increase in ethanol blends. One company is currently trying to market its product, while other companies are in the process of testing their formulations. These products have not been proved commercially yet.

## Carbon Monoxide Emissions and Oxygenated Fuels

Carbon monoxide results from incomplete combustion of fuel and is emitted directly from vehicular tailpipes. These conditions are common during vehicle startup when the air supply is restricted ("choked"), when cars are not tuned properly, and at altitudes where "thin" air reduces the amount of oxygen available for combustion.

EPA has estimated that the contribution to urban carbon monoxide pollution from motor vehicle emissions can exceed 90 percent in urban areas. The approaches taken to reduce mobile CO emissions include improving catalytic converter designs, incorporation of onboard computer and emission sensors, and using oxygenated fuels to lean out the air-to-fuel ratio.

Carbon monoxide emissions from automobiles increase dramatically in cold weather. This happens because cars need more fuel to start at cold temperatures and because some emission control devices (such as oxygen sensors and catalytic converters) operate less efficiently at colder temperatures. Recognizing that CO pollution is related to temperature, the Clean Air Act requires winter gasoline to contain an average oxygen concentration of at least 2.7 weight percent in CO nonattainment areas. Ten-percent ethanol blends can be used to obtain an oxygen concentration of 3.5 weight percent.

The benefit of an added oxygenate is greatest with older cars or off-road vehicles that operate with open loop technology. Engines in these vehicles do not have the capability to dynamically alter the intake air-to-fuel ratio. Newer cars use a closed loop technology that adjusts the air-to-fuel ratio in response to the composition of the exhaust stream. An onboard computer can increase the air ratio of the intake mixture, if the concentration of carbon monoxide in the exhaust is too high. Oxygenates can still provide some benefit in newer cars, especially during the warm up period. The exhaust feedback sensors work best when a stable operating temperature has been reached.

Ethanol is used in about 80 percent of the oxygenated fuels program in the U.S. At the same oxygen concentration only about half as much ethanol has to be used as MTBE, giving ethanol an economic advantage at current market prices.

The oxygenated fuel program has been very successful in reducing urban CO emissions. However, this program is starting to wind down as most areas, except the southern California basin, are expected to be in CO compliance by 2005. Also, the CO emission reductions from the use of oxygenated fuels will change as the vehicle fleet composition changes over time. The EPA used the MOBILE6 model to estimate this effect. The results shown in the accompanying table show that oxygenated fuels can contribute to significant reductions in CO emissions through 2005, but, by 2010, they are projected to have little impact.

**Table 7. Percent Reduction in CO Emissions Resulting from 3.5 Percent Oxygen, as Predicted by the MOBILE Model**

Year	MOBILE6
1997	10% to 20%
2000	5% to 15%
2005	0% to 10%
2010	0% to 2%

Source: U.S. Environmental Protection Agency

## **California Study on the Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline**

On March 25, 1999, Governor Gray Davis issued Executive Order D-5-99 calling for the removal of methyl tertiary-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states that the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. OEHHA looked at the air quality impacts of two MTBE replacement alternatives in California RFG: (1) ethanol, in the case of oxygenated gasoline and (2) alkylates, in the case of non-oxygenated gasoline.

The final report on the *Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline* issued in December 1999 concluded no degradation of air quality benefits would result from using either ethanol or alkylates to replace MTBE in California RFG. The report addressed the major concerns that have been raised about potential degradation of air quality from using ethanol. These can be briefly summarized as increases in evaporative emissions caused by the RVP increase of ethanol blends, increased emissions of acetaldehyde and PAN, and the potential for commingling of ethanol and non-ethanol containing gasoline in vehicular gas tanks.

OEHHA found that ethanol containing gasoline complying with California RFG standards would not cause increases in acetaldehyde and PAN emissions. OEHHA also found that evaporative emissions would not increase, because California RFG is RVP controlled. The report noted that a previous California study concluded that a one-psi RVP waiver for ethanol blends would result in an increase in ozone-forming potential due to greater evaporative emissions. Gas tank commingling was considered to be a potential problem only if the RFG oxygenate mandate is repealed. However, the extent of the problem is not well understood at this time and further research is needed.

Listed below are four of the findings from the California OEHHA report, along with some comments.

*1. In comparison to the non-MTBE components of gasoline, the atmospheric formation of toxic compounds from ethanol and alkylates is relatively slow.*

The maximum estimated outdoor air quality levels of ethanol and alkylates are at least a factor of 10 below any level of concern identified by OEHHA, so the main issues are their products of incomplete combustion and atmospheric transformations. The major products of concern for ethanol are acetaldehyde (a toxic air contaminant) and peroxyacetyl nitrate (PAN, an eye irritant and cause of plant damage). These compounds are offset by reductions in formaldehyde (a toxic air contaminant) due to the elimination of MTBE. Alkylates eventually form acetaldehyde, formaldehyde, and PAN, as do many other existing components of gasoline.

*2. The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with a Reid vapor pressure (RVP) greater than the summertime California limit of 7.0 pounds per square inch (psi) and increased evaporative emissions of volatile organic compounds (VOCs). This effect will be mitigated by RVP reductions in the California Phase 3 Reformulated Gasoline (CaRFG3) regulations.*

If the RFG oxygenate waiver is granted, commingling will likely increase. Current estimates of the overall effect of commingling on RVP range from 0.1 to 0.4 psi increase, depending on assumptions for the market share of ethanol-containing gasolines, consumer brand/grade loyalty, and the distribution of fuel tank levels before and after refueling events. The CaRFG3 regulations require a 0.1 psi RVP decrease from CARFG2 standards to help mitigate the effect of commingling. The commingling studies to date are very cursory, and the Air Resources Board is conducting further research to gain a better understanding of the commingling effects.

*3. Ethanol-containing gasolines may lead to increases in evaporative emissions because rubber, plastics, and other materials are permeable to ethanol, and ethanol may reduce the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles. This issue has been addressed in the United States Environmental Protection Agency's (U.S. EPA's) recently adopted Tier 2 emission standards. However, the current on-road motor vehicle fleet (other than flexible-fueled vehicles operated on alcohol blends) is not fully controlled from the perspective of evaporative ethanol emissions. Further research is needed to compare the effects of ethanol, MTBE (which also reduces the working capacity of charcoal canisters), and alkylates on evaporative emission from the existing California vehicle fleet.*

This conclusion encompasses several issues. Except for Ethanol FFVs, motor vehicles, are not required certified their emission systems on ethanol fuels. Ethanol FFVs are certified on E85, pure gasoline, and E10 (highest RVP increase). They must meet evaporative emissions standards for all three blends. The Tier 2 rules address a different issue. EPA was concerned that some manufacturers are using materials in the nonmetallic portion of the fuel system that could unacceptably degrade if ethanol fuels are used. In particular, the permeability of elastomer components could increase in the presence of alcohol. This is a slow process that might take place over a period of years. EPA is requiring manufactures to use E10 during the durability cycle, a process that can be likened to driving a vehicle 50 or 100 thousand miles to age components. The vehicle is then certified to meet emission standards on gasoline, not E10. The Tier 2 requirements address the potential for ethanol to degrade nonmetallic fuel components. It does not require that a vehicle be certified for evaporative emissions on E10.

*4. So long as the CaRFG3 regulations address the potential for ethanol to increase evaporative emissions and cause more rail and truck traffic, the substitution of ethanol and alkylates for MTBE in California's fuel supply will not have any significant air quality impacts. This finding is supported by theoretical calculations in the South Coast Air Basin using state-of-the-science tools, an analysis of the impact of uncertainties, air quality measurements in areas that have already introduced ethanol into their fuel supply, and an independent scientific peer review by the University of California.*

The report also provided the following summary of the differences in emissions between complying California fuels containing MTBE, ethanol, and no oxygenates. Both the 1997 and 2003 baseline MTBE baseline fuels meet CARFG 2 standards. The 1997 MTBE baseline gasoline is representative of gasoline used in 1997; the 2003 MTBE baseline gasoline assumes further emission reductions are achieved. Two ethanol concentrations were analyzed, one containing 2.0 wt% oxygen (E5.7) and one containing 3.5 wt% oxygen (E10). Both ethanol blends and the non-oxygenated gasoline meet the CARFG3 standards.

All pollutants of concern decrease from the 1997 MTBE baseline to the 2003 fuels due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for formaldehyde and acetaldehyde to 33% for benzene and 43% for 1,3-butadiene. Several differences exist among the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios.

- Since fuel-related activities are the only inventoried source of MTBE, levels of MTBE decrease 100% for the ethanol-blended and non-oxygenated gasolines.
- Ethanol levels for the ethanol-blended gasolines increase by 48% (2.0 wt% oxygen fuel) and 72% (3.5 wt% oxygen fuel), but acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen.
- PAN levels are not predicted to increase for either the ethanol-blended or non-oxygenated gasolines.
- Benzene levels increase slightly (1%) for the ethanol-blended gasoline at 3.5 wt% oxygen, with decreases predicted for the other two gasolines.
- All three MTBE-free gasolines produce modest reductions in 1,3-butadiene (2%) and formaldehyde (2 to 4%) levels and essentially no change in ozone, nitrogen dioxide, nitric acid, and PPN (peroxypropionyl nitrate) levels.
- As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average carbon monoxide levels (3%) and the 3.5 wt% oxygen ethanol-blend in lower carbon monoxide values (-9%). These are summertime levels, a time period when violations of the standard do not occur.
- Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide levels within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

## **Greenhouse Gas Emissions**

The prospect for global warming from anthropogenic activities is a growing concern in the international community. The combustion of vast quantities of fossil fuel used to satisfy our appetite for energy has released enormous quantities of carbon dioxide into the atmosphere. This excess blanket of carbon dioxide traps heat from incoming solar radiation much like a greenhouse. About 35 percent of the carbon dioxide emissions from energy use in the United States come from the transportation sector.

Other gaseous emissions besides CO<sub>2</sub> contribute to global warming. The Intergovernmental Panel on Climate Change (IPCC) assigns weighting factors to CO<sub>2</sub> (1), CH<sub>4</sub> (21), and N<sub>2</sub>O (31) to indicate their global warming potential relative to CO<sub>2</sub> (weighting factors in parenthesis). These emissions are not classified by EPA as contributing to urban air quality problems. Other emissions, such as CO, VOCs, and NO<sub>x</sub> are also recognized as greenhouse gases, but are not yet assigned weighting factors by the IPCC. These emissions are causes of urban air quality problems.

Both corn and cellulosic ethanol produce less GHG emissions than gasoline. Biofuels reduce the net carbon emissions to the atmosphere because the carbon dioxide released during biofuel combustion comes from carbon dioxide withdrawn from the ambient environment during the growth stage of the feedstock plants. The GHG reductions for corn ethanol are modest. Cellulosic ethanol, on the other hand, offers a unique opportunity for releasing virtually no net GHG emissions, since the biomass-to-ethanol conversion process makes extensive use of renewable energy.

### **The Fuel Cycle**

To properly account for carbon emissions associated with a particular fuel, the entire fuel cycle must be considered. For biomass ethanol, this includes feedstock production, ethanol conversion, feedstock and ethanol transportation, and fuel combustion. Because biomass ethanol is a renewable fuel, the carbon released during fuel combustion comes from the carbon withdrawn from the biosphere during feedstock growth. Consequently, vehicular combustion of biofuels produces zero net carbon dioxide emissions. However, farming and ethanol conversion produce GHG emissions.

A major difference between cellulosic and corn ethanol conversion processes is their source of power. Corn ethanol plants rely heavily on fossil sources. Cellulosic ethanol plants, on the other hand, have an integrated power plant that uses the lignin in the feedstock for process power. Because most of the energy requirements associated with cellulosic ethanol are derived from renewable sources, the conversion process releases practically no net carbon dioxide.

The ethanol conversion process produces other products besides ethanol, and the GHG emissions associated with these coproducts have to be accounted for. Cellulosic ethanol produces electricity as a coproduct. Corn ethanol produces animal feed products (both dry and wet milling) and corn syrups and sweeteners (wet milling).

The treatment of GHG emissions associated with ethanol coproducts has evolved over time. Both Mark Delucchi and Michael Wang, who have developed the two most widely accepted models for estimating GHG emissions from transportation fuels, currently favor the product displacement approach. In this approach, all GHG emissions associated with the combined ethanol / coproduct production process are first allocated to ethanol and then adjusted for the GHG emissions associated with the market products displaced by the coproducts. For corn ethanol, this involves first determining what animal feed products displaced by the corn ethanol coproducts and then calculating the GHG emissions that would have been emitted if they were produced. For cellulosic ethanol, excess electricity generated at the ethanol plant is sold to outside users. This displaces electricity that would have been produced by other power plants. Other techniques have also been used to distribute GHG emissions between ethanol and the coproducts, such as allocating the GHG emissions of a shared process according to the process energy used to produce the ethanol versus the coproducts.

### **GHG Emission Reductions**

A 1999 Argonne National Laboratory report estimated that corn ethanol used in E10 currently reduces GHG emissions between 12 and 19 percent relative to gasoline, depending on whether wet or dry milling is used. By 2005, GHG emission reductions for corn ethanol are projected to increase to between 24 and 26 percent. Increased emission reductions are due to advances in farming practices and ethanol conversion technologies. In 2005, cellulosic ethanol used in E10 is projected to reduce GHG emissions between 84 and 130 percent, depending on whether herbaceous or woody biomass is used. Reductions more than 100% are explained by a coproduct credit for the sale of electricity from cellulosic ethanol plants. Among transportation fuels, cellulosic ethanol provides the greatest GHG benefit, except for methane from landfill gases. However, the potential from landfills is limited. Most methane comes from natural gas.

**Table 8. Reduction in Greenhouse Gas Emissions (grams/mile) from Ethanol Used in Ethanol Blends (percentage relative to gasoline, percent range represents E10 to E95)**

<b>Corn – Current</b>	
<b>Dry Mill</b>	<b>19% - 28%</b>
<b>Wet Mill</b>	<b>12% - 27%</b>
<b>Corn – Near Future (2005)</b>	
<b>Dry Mill</b>	<b>26% - 35%</b>
<b>Wet Mill</b>	<b>24% - 32%</b>
<b>Cellulosic – Near Future (2005)</b>	
<b>Woody Biomass</b>	<b>130% - 127%</b>
<b>Herbaceous Biomass</b>	<b>84% - 86%</b>

Source: M. Wang, C. Saricks, D. Santini, *Effects of Fuel Ethanol Use on Fuel-Cycle Energy and greenhouse Gas Emissions*, ANL/ESD-38, January 1999